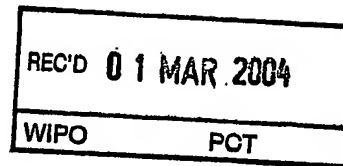


PRV

PATENT- OCH REGISTRERINGSVERKET
Patentavdelningen

PCT / SE 2004 / 0 0 0 1 7 3



Intyg Certificate

Härmed intygas att bifogade kopior överensstämmer med de handlingar som ursprungligen ingivits till Patent- och registreringsverket i nedannämnda ansökan.

This is to certify that the annexed is a true copy of the documents as originally filed with the Patent- and Registration Office in connection with the following patent application.



(71) Sökande Tetra Laval Holdings & Finance SA, Pully CH
Applicant (s)

(21) Patentansökningsnummer 0300554-3
Patent application number

(86) Ingivningsdatum 2003-02-28
Date of filing

Stockholm, 2004-02-19

För Patent- och registreringsverket
For the Patent- and Registration Office

Marita Öun
Marita Öun

Avgift
Fee

**PRIORITY
DOCUMENT**
SUBMITTED OR TRANSMITTED IN
COMPLIANCE WITH RULE 17.1(a) OR (b)

PATENT- OCH
REGISTRERINGSVERKET
SWEDEN

Postadress/Adress
Box 5055
S-102 42 STOCKHOLM

Telefon/Phone
+46 8 782 25 00
Vx 08-782 25 00

Telex
17978
PATOREG S

Telefax
+46 8 666 02 86
08-666 02 86

A BINDER AND A PACKAGING LAMINATE COMPRISING THE BINDER

TECHNICAL FIELD

The present invention relates to a binder to be used in a packaging laminate, especially a packaging laminate comprising a silicon oxide layer. The invention also relates to the packaging laminate comprising the binder.

PRIOR ART AND PROBLEMS

US 5,731,092 discloses a packaging material comprising a film covered with silicon oxide and a polyolefin film, wherein a binder arranged between the silicon oxide and the polyolefin film is selected from the group consisting of polyolefins grafted with unsaturated alkoxysilanes, polyolefins grafted with unsaturated epoxides, and copolymers of ethylene and of at least one unsaturated epoxide. The grafted polyolefin binder is arranged as a binding layer in contact with the silicon oxide layer and binding the same to the polyolefin film.

Although it has been shown that the grafted polyolefin as such, according to US 5,731,092, provides for a good adhesion to silicon oxide, it has now been found that the internal adhesion in a packaging laminate, between a silicon oxide layer and an adjacent layer, such as the mentioned polyolefin film, when using the grafted polyolefin in a binding layer therebetween, does not get as good as would be expected. Accordingly, undesirable delamination may occur, through failure of the binding layer.

DISCLOSURE OF THE INVENTION

It is, therefore, an object of the present invention to overcome or alleviate the above-described problem related to adhesion of a binding layer comprising a grafted polyolefin, arranged between a silicon oxide layer and an adjacent layer, in a packaging laminate

One object of the invention is to provide a binder for a packaging laminate, which binder comprises a polyolefin grafted with an unsaturated alkoxy silane, in essence according to US 5,731,092, but which binder provides for improved adhesion between a silicon oxide layer and an adjacent layer, in a packaging laminate.

Another object is to provide a packaging laminate comprising a binding layer of such a binder, arranged between a silicon oxide layer and an adjacent layer, in the packaging laminate, which packaging laminate is improved in respect of delamination properties, mainly at wet conditions, i.e. which packaging laminate can not be delaminated in the binding layer at wet conditions. The packaging laminate according to the invention may be converted into a sealed package for food products, preferably liquid food products.

These and other objects are achieved by the binder and the packaging laminate according to the appended claims.

More specifically, it has now been found that the grafted polyolefin binder of US 5,731,092 can be improved in respect of its adhesion properties if being blended with a non-grafted polyolefin.

Surprisingly, it has been found that the number of adhesion points between the grafted sites in the binder and the silicon oxide can be vastly increased if the grafted polyolefin is blended with a non-grafted polyolefin, i.e. the number of adhesion points increases despite less grafted sites in the binder polymer!

The invention is based on the insight that it is not only the number of grafted sites that affects the degree of adhesion, but also their ability to physically come in contact with the silicon oxide. It has been found that the grafting of polyolefin according to US 5,731,092 results in a cross-linking of the polyolefin, which makes the polyolefin less flexible than the non-grafted polyolefin. Due to the impaired flexibility of the grafted polyolefin, the number of contact points between the binding layer composed of the grafted polyolefin and the silicon oxide will be less than for a binding layer solely composed of a non-grafted polyolefin of the same type. However, in a binding layer solely composed of a non-grafted polyolefin, the adhesion in an individual adhesion point of the plurality of adhesion points will not be as good as in an individual adhesion point of a binding layer composed solely of a grafted polyolefin.

The present invention solves the problem related to these contradictory aspects of grafted and non-grafted polyolefin binders, by providing a binder that is a blend of a grafted polyolefin and a non-grafted polyolefin. Here, the improved flexibility that is achieved due to the presence of a non-grafted polyolefin provides for an increased number of adhesion points, while the grafted polyolefin provides for improved adhesion in those points, all in all resulting in adhesion properties that are better than the adhesion properties of a grafted polyolefin binder per se and a non-grafted polyolefin binder per se.

According to one aspect of the invention, the polyolefins which are grafted with alkoxysilanes are chosen from the group that consist of:

homopolymers of ethylene or of propylene;

copolymers of ethylene and of vinyl acetate;

copolymers of ethylene and of at least one alkyl(meth)acrylate. The alkyl groups of the alkyl(meth)acrylate has up to 10 carbon atoms and can be linear, branched or cyclic. Mention may be made, by way of illustration of the alkyl(meth)acrylate, of in particular n-butyl acrylate, methyl acrylate, isobutyl acrylate, 2-ethylhexyl acrylate, cyklohexyl acrylate, methyl methacrylate or ethyl methacrylate. Preference is given, among these (meth)acrylates, to ethyl acrylate, methyl acrylate, n-butyl acrylate and methyl methacrylate;

copolymers of ethylene and of an alpha-olefin such as butene or hexane; amorphous poly(alpha-olefin)s (APAO). Use is preferably made of the APAOs derived from ethylene, propylene, butene or hexane. Use is advantageously made either of ethylene-propylene-butene copolymers with a high butene content or of ethylene-propylene-butene copolymers with a high propylene content or of homo- or copolymers of butene.

Use is advantageously made of ethylene-alkyl(meth)acrylate copolymers.

Most preferably, said grafted polyolefin and said non-grafted polyolefin are polyolefins of the same type, according to the above, preferably polyethylene type polyolefins.

Mention may be made, among alkoxysilanes carrying an unsaturation, of:
 $\text{CH}_2=\text{CH}-\text{Si}(\text{OR})_3$, vinyltrialkoxysilanes
 $\text{CH}_2=\text{CH}-\text{CH}_2-\text{Si}(\text{OR})_3$, allyltrialkoxysilanes
 $\text{CH}_2=\text{CR}_1-\text{CO}-\text{O}-\text{Y}-\text{Si}(\text{OR})_3$

(meth)acryloxyalkyltrialkoxysilanes (or (meth)acrylsilanes) in which:

R is an alkyl having from 1 to 5 carbon atoms or an alkoxy $-R_2OR_3$ in which R_2 and R_3 are alkyls having at most 5 carbon atoms for the combined units R_2 and R_3 ;

5 R_1 is a hydrogen or methyl;

Y is an alkylene having from 1 to 5 carbon atoms.

Use is made, for example, of vinylsilanes, such as trimethoxyvinylsilane, triethoxyvinylsilane, tripropoxyvinylsilane, tributoxyvinylsilane, triethoxyvinylsilane or tris(β -methoxyethoxy)vinylsilane, allylsilanes, such as
10 trimethoxyallylsilane, triethoxyallylsilane, tripropoxyallylsilane, tributoxyallylsilane or triethoxyallylsilane, or acrylsilanes, such as acryloxymethyltrimethoxysilane, methacryloxymethylmethoxysilane, acryloxyethyltrimethoxysilane, methacryloxyethyltrimethoxysilane, acryloxypropyltrimethoxysilane, methacryloxypropyltrimethoxysilane, acryloxybutyltrimethoxysilane,
15 methacryloxybutylmethoxysilane, acryloxyethyltriethoxysilane, methacryloxyethyltriethoxysilane, methacryloxyethyltripropoxysilane, acryloxypropyltributoxysilane or methacryloxypropyltripentoxysilane.

It is also possible to use mixtures of these products.

Use is preferably made of:

20 $CH_2=CH-Si-(OCH_3)_3$, vinyltrimethoxysilane (VTMO)

$CH_2=CH-Si-(OCH_2CH_3)_3$, vinyltriethoxysilane (VTEO)

$CH_2=CH-Si(OCH_2OCH_2CH_3)_3$ vinyltrimethoxyethoxysilane (VTMOEO)

and (3-(methacryloxy)propyl)trimethoxysilane $CH_2=C(CH_3)-CO-O-(CH_2)_3-Si(OCH_3)_3$.

25 The polyolefins can be grafted in the molten state in the presence of radical initiator(s).

The grafting reaction is carried out in a single- or twin-screw extruder feed with polyolefins in a feed hopper, for example in the form of granules; the polyolefins are melted by heating in a first region of the extruder and, in a second
30 region, the reactants are introduced into the molten mass of the polyolefins.

The radical initiators can be chosen from peroxides, peracids, peresters or peracetals. They are generally used in the proportion of 0.01% to 0.5% by mass with respect to the polyolefins to be grafted.

Mention may be made, by way of example, of:

dicumyl peroxide (DICUP),

2,5-dimethyl-2,5-di(tert-butylperoxy)hexane (DHBP), α,α' -(di-tert-butylperoxyisopropyl)benzene (Y1490).

5 It is preferable to dissolve the radical initiator in the liquid vinylalkoxysilane before introducing them, for example by means of a metering pump, into the polyolefins in the molten state.

It is preferable for the region for introduction of the reactants to be sufficiently long and at a sufficiently low temperature to ensure good dispersion of
10 the reactants and the smallest possible thermal decomposition of the radical initiator.

The grafting reaction proper takes place in a third region of the extruder at a temperature capable of providing for complete decomposition of the radical initiator; before the exit of the molten mass at the extruder head, a degassing
15 region is provided for where the decomposition products from the initiator and the unreacted vinylsilane are degassed, for example under vacuum.

The grafted polyolefins are recovered at the extruder outlet, for example in the form of granulated rods, after cooling under cold air.

The ratio by weight of the grafts to the grafted polymer is generally
20 between 0.1 and 5 % and preferably 0.15 to 2.5 %.

According to one aspect of the invention, the binder comprises 30 – 70 %, preferably 40 – 60 % and even more preferred 45 – 55 % by weight of the grafted polyolefin.

According to another aspect of the invention, the binder may be constituted
25 of a dry blend of the grafted polyolefin and the non-grafted polyolefin. This may be realized for example by dry blending grafted polyolefin granules with non-grafted polyolefin granules, such that they will melt together in connection with the melting when the binder is applied as a binding layer in the packaging laminate, by extrusion e.g.

30 On the other hand, the binder may be constituted of a compound blend of the grafted polyolefin and the non-grafted polyolefin, i.e. the grafted and non-grafted polyolefins being intimately blended with each other, at molecular level, already before the binder is melted in connection with the application of the

binder as a binding layer in the packaging laminate. This may be realized for example by individual granules being produced, that are composed of a blend of the grafted polyolefin and the non-grafted polyolefin.

5 The invention also relates to a packaging laminate comprising a film covered with silicone oxide, which packaging laminate comprises a binder according to the above, which binder is arranged as a binding layer, to bond the silicon oxide to an adjacent layer, in the laminate.

The film covered with silicon oxide is preferably a film of polyester or poly-
amide, preferably a film of a polymer selected from mono- or biaxially oriented
10 polyethyleneterephthalate (PET), mono- or biaxially oriented polyethylenenaphte-
nate (PEN), mono- or biaxially oriented polyamide (PA) or mono- or biaxially
oriented polybutylene terephthalate (PBT).

The adjacent layer, to which the silicon oxide is bonded by the binder, may
be a polyolefin film, made e.g. of polyethylene, polypropylene or copolymers of
15 ethylene, such as, for example, ethylene-propylene, ethylene-butene, ethylene-
hexene, ethylene-alkyl(meth)acrylate or ethylene-vinyl acetate copolymers. The
choice of the material for this layer may provide for a transparent packaging
laminate, to be used e.g. in a transparent pouch for food. However, according to
another embodiment of the packaging laminate, the adjacent layer may
20 alternatively be composed essentially of paper or paperboard.

According to one aspect of the invention, the binding layer in the
packaging laminate, composed by the inventive binder, amounts to 2-35 g/m²,
preferably 5-30 g/m² and even more preferred 10-25 g/m², calculated on dry
matter.

25 According to one embodiment of the packaging laminate, the binding layer
composed of the inventive binder may be extruded to constitute a sole binding
layer between the silicon oxide and the adjacent layer, in which case the binding
layer preferably amounts to at least 10 g/m², preferably 10-35 g/m², more prefe-
rably 10-30 g/m² and even more preferred 10-25 g/m², calculated on dry matter.

30 According to another embodiment of the packaging laminate, the binding
layer composed of the inventive binder may be co-extruded together with a
polyolefin layer that is free from said grafted polyolefin, the binding layer being
disposed in contact with the silicon oxide. In this case, it may suffice to have a

binding layer composed of the inventive binder, that amounts to 2-20 g/m², preferably 2-15 g/m² and even more preferred 2-10 g/m², calculated on dry matter. The polyolefin that is co-extruded together with the binding layer composed of the inventive binder, is preferably a polyolefin of the same type as the grafted and
5 non-grafted polyolefin of the binder, most preferably a polyethylene polyolefin.

DESCRIPTION OF THE DRAWINGS

Further advantages and favourable characterising features of the present invention will be apparent from the following detailed description, with reference
10 to the appended figures, in which:

Fig. 1 is a cross-sectional view of a preferred laminated packaging material according to the present invention, and

Fig. 2 is a cross-sectional view of a another embodiment of a laminated packaging material according to the present invention,

15 Fig. 3 is a cross-sectional view of a transparent laminated packaging material according to the present invention.

Fig. 1 thus shows a packaging laminate 10, comprising a first polymer carrier layer 11a being a film of a preferably oriented polyester, such as for example polyethyleneterephthalate (PET), or a film of a preferably oriented
20 polyamide (PA), onto which is coated a thin gas barrier layer of SiOx 13a by means of plasma enhanced chemical vapour deposition (PECVD).

The thickest layer in the laminate is a bulk paper or paperboard layer 15. It is directly bonded to the SiOx layer 13a, by means of a binding layer 18a. In the binding layer 18a in contact with the layer of SiOx 13a and the paper or paperboard layer 15, there is used a blend of a polyethylene base polymer graft
25 modified by an unsaturated alkoxysilane compound, and a corresponding non-grafted polyethylene polymer, which provides for exceptionally good adhesion between the SiOx layer 13a and the paper or paperboard layer 15. The binding layer 18a typically has a basis weight of 5-30 g/m², in this embodiment of the
30 invention.

On the outside of the paper or paperboard layer 15, which will constitute the outside wall of a packaging container produced from the packaging laminate,

is applied a first outermost layer 16 of a heat-sealable polyolefin, preferably a low density polyethylene (LDPE) or a linear low density polyethylene (LLDPE), which include also so-called metallocene-catalysed LLDPE's (m-LLDPE), i.e. LLDPE polymers catalysed by means of a single site catalyst. Other examples of
5 alternative polymers for the outside packaging wall layer may be medium high density polyethylene (MDPE) or polypropylene (PP).

On the outside of the polymer carrier layer 11a, which will constitute the inside wall of a packaging container produced from the packaging laminate, is applied a second layer 17a of a heat-sealable polyolefin, preferably comprising a
10 metallocene polyethylene material. Preferably, a third layer 17b of a heat-sealable polyolefin is arranged in direct contact with the second layer 17a of a heat-sealable polyolefin and is preferably co-extruded together with it, but beneficially at a higher temperature. Hence, the third layer 17b of a heat-sealable polyolefin is arranged between the polymer carrier layer 11a and the second layer
15 17a of a heat-sealable metallocene polyolefin. Preferably, the third layer of a heat-sealable polyolefin is a layer of LDPE, optionally LLDPE.

Fig. 2 shows a packaging laminate 30 according to another embodiment of the invention. The only difference in relation to the packaging laminate 10 of Fig. 1, is that the binding layer 18a, comprising a blend of a grafted and a non-grafted
20 polymer, is thinner (typically 2-15 g/m²) and instead complemented by a complementary binding layer 22 of non-grafted polyolefin polymer. Preferably, the two binding layers 18a and 22 have been co-extruded. In this way, the binding layer 18a of grafted and non-grafted blend provides for exceptionally good adhesion to the SiOx layer 13a, to which it faces directly, while the complementary binding
25 layer 22 keeps costs down and still ensures that enough total binding layer is present.

Fig. 3 shows a transparent packaging laminate 50, comprising a first and second carrier layer 11a, 11b in accordance with the above, onto which are coated thin gas barrier layers of SiOx 13a, 13b. The two SiOx layers are
30 preferably directed towards the interior of the laminate, thus facing each other. Between the two carrier layers coated with gas barrier layers, is laminated an intermediate layer 23 of a relatively stiff olefin polymer, such as for example high density polyethylene (HDPE) or polypropylene (PP). The intermediate layer is

thicker than any of the surrounding layers in the packaging laminate, and provides as such a distancing element between the two carrier layer films of oriented polymer. The preferred oriented polymer films have a certain degree of inherent stiffness in that they are oriented and thus may have a relatively higher degree of crystallinity than non-oriented polymer films. The olefin polymer of the intermediate layer also contributes with a certain degree of stiffness by itself to the packaging laminate as a whole. The so-called I-beam arrangement of two relatively stiff carrier layers laminated on each side of a thicker and relatively stiff intermediate polymer layer provides for a laminate having surprisingly good bending stiffness in relation to its thickness. In addition, the arrangement of the two PECVD-deposited SiOx-layers has proved to result in a much more than two-fold increased gas barrier, compared to a laminate or film containing merely one SiOx-layer. Thus, the arrangement of an intermediate layer also acting as a "buffer" for penetration of gas, in particular oxygen gas, provides for surprisingly improved gas barrier properties, which indicates a synergistic effect resulting from this particular arrangement.

Layers 16, 17a, 17b, 20a and 20b correspond to the layers having the same reference number in Fig. 1 and Fig. 2. (Layer 20b is of the same type as layer 20a). The binding layers 18a and 18b correspond to the binding layer 18a in Fig. 1. It is also conceivable, although not shown, that one or both of these binding layers 18a, 18b are co-extruded together with a complementary binding layer of non-grafted polyolefin polymer, as shown in Fig. 2.

By way of conclusion it should be observed that the present invention which has been described above with particular reference to the accompanying drawings, is not restricted to these embodiments described and shown exclusively by way of example, and that modifications and alterations obvious to a person skilled in the art are possible without departing from the inventive concept as disclosed in the appended claims.

CLAIMS

1. A binder for a packaging laminate, which binder comprises a polyolefin grafted with an unsaturated alkoxysilane, characterised in that said grafted polyolefin is blended with a non-grafted polyolefin, in said binder.
2. A binder according to claim 1, characterised in that said grafted polyolefin and said non-grafted polyolefin are polyolefins of the same type, preferably polyethylene type polyolefins.
3. A binder according to claim 1 or 2, characterised in that it comprises 30 – 70 %, preferably 40 – 60 % and even more preferred 45 – 55 % by weight of the grafted polyolefin.
4. A binder according to any one of the preceding claims, characterised in that said binder is constituted by a dry blend of said grafted polyolefin and said non-grafted polyolefin.
5. A binder according to any one of the preceding claims, characterised in that said binder is constituted by a compound blend of said grafted polyolefin and said non-grafted polyolefin.
6. A packaging laminate (10, 30) comprising a film (11a) covered with silicone oxide (13a), characterised in that it comprises a binder (18a) according to any one of claims 1-5, which binder is arranged to bond the silicon oxide to an adjacent layer, in the laminate.
7. A packaging laminate according to claim 6, characterised in that said binder (18a) is present in an binding layer of 2-35 g/m², preferably 5-30 g/m² and even more preferred 10-25 g/m²,

11

calculated on dry matter.

8. A packaging laminate according to any one of claims 6 and 7, characterised in that said binding layer (18a) is co-extruded together with a polyolefin layer (22) that is free from said grafted polyolefin, the binding layer (18a) being disposed in contact with the silicon oxide (13a).

ABSTRACT

5 A binder for a packaging laminate, which binder comprises a polyolefin grafted with an unsaturated alkoxysilane. According to the invention, the grafted polyolefin is blended with a non-grafted polyolefin, in said binder, whereby the flexibility of the binder is improved, which in turn provides for an increased number of adhesion points when the binder is used in a binding layer in the packaging laminate. The invention also relates to packaging laminate (10, 30) comprising the binder.

10

Publication figure: 1

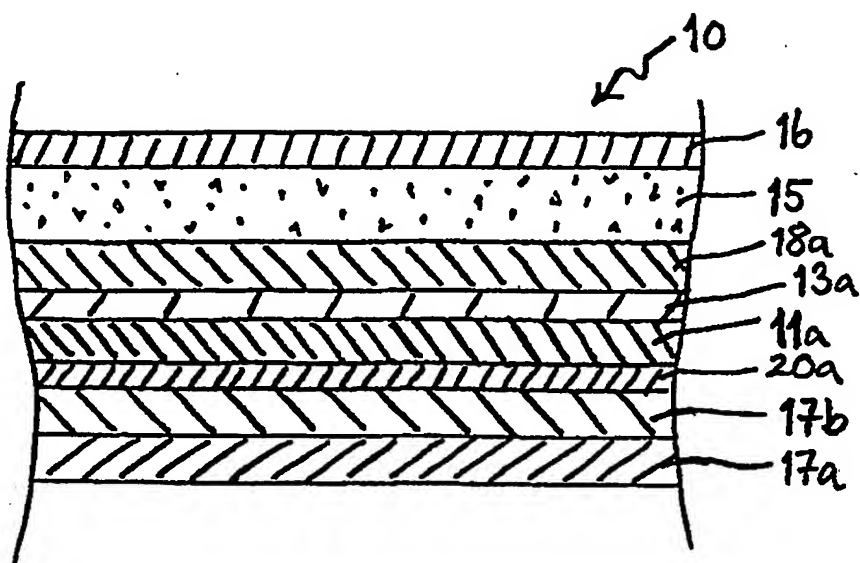


Fig. 1

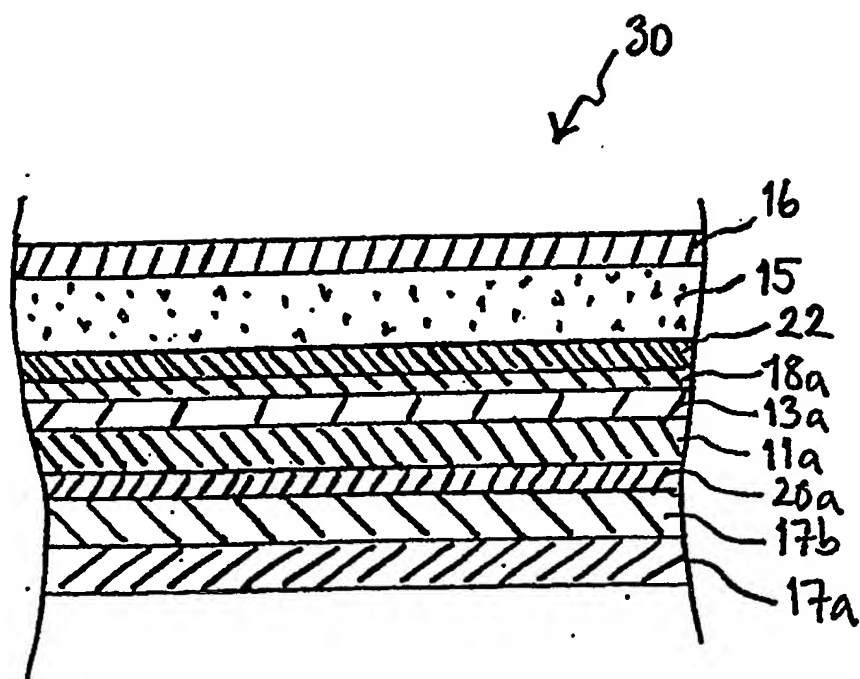


Fig. 2

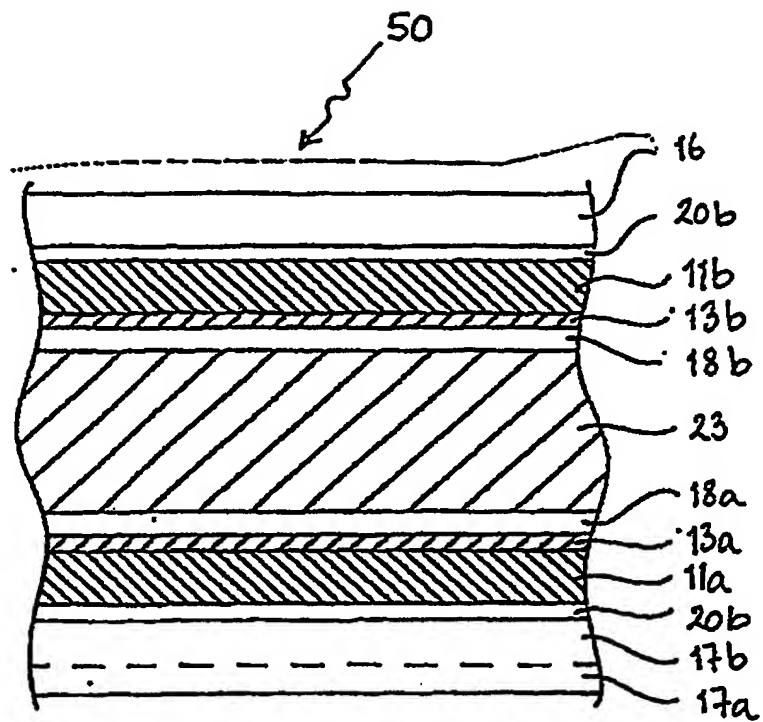


Fig. 3